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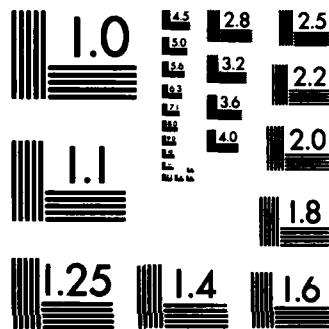
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ONR LONDON CONFERENCE REPORT

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THE 10TH INTERNATIONAL THERMAL SPRAYING CONFERENCE

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16 August 1983

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THE 10TH INTERNATIONAL THERMAL SPRAYING CONFERENCE

Thermal-sprayed protective coatings are playing vital roles in an increasingly wide range of industries. Thermal spraying, the spray deposition of molten materials, is both economical and highly versatile. Many materials--ranging from plastics to metals to refractory ceramics--can be melt-spray deposited onto substrates to be protected, usually with only limited heating of the substrate.

Thermal spraying is a highly specialized technique, calling for an interesting mix of voodoo and solid engineering. The practitioners of the art and science attended the International Thermal Spray Conference '83 (ITSC-83), which convened in Essen, Germany, from 2 through 6 May 1983. The conference, organized under the auspices of the International Institute of Welding and held every 3 years, attracted 400 attendees from 26 countries. Some 80 papers covered the field, from processing methodology to the behavior of coatings under severe environmental conditions. (The appendix lists the speakers and their papers.) The proceedings, in English, are available from the Deutscher Verband für Schweisstechnik e.V., Postfach 2725, D-4000 Düsseldorf, Germany.

This writer reported on the previous conference in the series, ITSC-80, which was organized by the Dutch Welding Society in The Hague (see ONR London Conference Report C-4-80, 9 September 1980). During the last few years there have been many changes in thermal spraying, and most of the conference papers were substantial engineering contributions. ITSC-83 was both a scientific-engineering conference and a trade show, and thus provided a rather good view of where the field stands today and where it appears to be moving.

Plenary Address

"Future Aspects of Thermal Spraying" was the subject of the plenary address given by the conference chairman, H.D. Steffens, professor at Dort-

mund Univ. Steffens reviewed the major developing aspects of the three techniques of thermal spraying: flame, electric-arc, and plasma spraying. It should be pointed out that thermal-sprayed coatings, prepared under normally accepted procedures, are relatively porous and have rough surfaces. Special techniques and care will significantly reduce such deficiencies, as will be discussed below.

Flame spraying, the mainstay of the field, involves the melting of powder or wire by a gas-oxygen fuel mixture, with atomization and projection by high velocity air originating from a compressor. A new development in this technique is the application of rocket technology to accelerate the particles to extremely high velocities, yielding coatings that have densities and substrate adhesion superior to those obtained from the usual flame spray method and, presumably, to those obtained by plasma spraying. The so-called "hypersonic flame spraying" has been applied to the deposition of cemented carbide, coatings much sought after by industry. The aircraft and hard facing industries, for example, have driven the development of the hypersonic gun; they want to compete with detonation-gun-formed ("D-gun") coating, a proprietary technique used by Union Carbide to create hard surfaces. In D-gun coating, a gas-oxygen fuel mixture is fired at frequent intervals (more than five times a second); the powder to be deposited is injected into travelling supersonic shock waves and accelerated to high velocities to form dense, well-adhered coatings. The Russians, in fact, have developed such a gun and have written widely about its design and details of operation. A more recent US-based D-gun entry is labeled the "FARE-gun." While it shows promise, like hypersonic flame spraying, scientists have not proved whether it is competitive with D-gun-formed coatings.

Steffens, as well as other authors at the conference, discussed the use of thermal spraying methods, principally flame and electric-arc, to protect structures against corrosion. Active

metal coatings, such as flame or arc-sprayed zinc and aluminum or their alloys, on steel act cathodically as extended sacrificial anodes. That is, in electrolytes, the coating, being anodic to the steel substrates, conveys relative nobility to the steel, giving highly effective long-acting protection. The sprayed coatings can be primed and then sealed with a wide range of formulations, yielding exceptionally long term protection.

Barrier coating is another approach to corrosion-oxidation protection using thermal spraying. A protective coating is deposited to limit penetration of corrosive substances; thus, porosity severely limits the method. There are many ways to reduce or eliminate such porosity through special spray processes (e.g., low pressure spraying, post-spray treatment by laser or electron-beam surface melting). Such processes were outlined by Steffens and received attention at ITSC-83. Control of the environment in which thermal spraying is done can reduce the degree of oxides in the coating. In the first instance, simple shrouds can be used to exclude oxygen. Generally, the working plasma gas is argon or an argon-hydrogen mixture. It is possible to shield the gun so that air is continuously shrouded from the flame and from the immediate area of the work piece, where particle impingement occurs. The gun can be hand held or handling equipment can be used. An obvious extension of the shroud involves flushing an entire chamber with inert gas, thus enabling the spraying of large or complex-shaped substrates. Considerable work has been done with such methods, and spraying in a controlled environment clearly yields denser, superior coatings, which behave exceptionally well in corrosive environments.

A major recent development involves plasma spraying under reduced pressure. The process is generally carried out in a water-cooled pressure vessel. Under standard operating conditions of plasma spraying, the pressure can be maintained at between 2 and 50 Torr. There are many benefits associated with spraying

at reduced pressures. For example, the oxide content is significantly reduced for low pressure sprayed coatings. In addition, velocity for a given power setting is substantially increased, yielding superior layering of the rapidly solidifying molten particles, which, ultimately, leads to densities approaching bulk.

Automation, a rapidly developing field, is entering thermal spraying technology due to the need to operate in a controlled environment and to achieve improved reproducibility. Clearly, at the 1986 conference there will be considerable interest in the use of robots in thermal spraying.

While low pressure plasma spraying has been developed and used principally by aircraft-related industries, the technique is now being applied more generally--for example, for hard facing with cemented carbides. The technology has grown rapidly during the past few years; several manufacturers and research laboratories have been developing the equipment required for its implementation.

Steffens described the use of lasers for the post-spray surface melting of metal coatings. The technique was the subject of a paper by H. Bhat et al. (State Univ. of New York [SUNY], Stony Brook); a continuous wave CO₂ laser was rastered onto a plasma sprayed Ni-based alloy coating. The laser melted the top 20 μ m of the coating surface, effectively sealing the coating and yielding dramatically improved corrosion-oxidation properties.

Conference Papers

The lecture given by Steffens set the theme for the conference, which concentrated on newer technical developments, together with some particularly good scientific evaluations of processing and coating properties. This discussion of the conference papers focuses on presentations related to the most active aspects of the field.

The first series of papers considered the substrate and went on to finishing processes. Substrate pretreat-

ments (e.g., grit blasting versus acid treatment versus Mo-band coating) were discussed by Japanese workers from Osaka Univ. and the Iron and Steel Technical College, Hyogo. The adhesion strength between a plasma-sprayed alumina coating and a prepared stainless steel substrate was related to electron spectroscopy for chemical analysis (ESCA) spectra and surface roughness of the substrate before spraying. The results of the study were complex but, overall, point to the influence of surface chemical state on adhesion. Further work from Osaka concentrated on post-spray grinding of self-fluxing Ni-Cr alloys. Bhat et al. examined the effects of laser treatment on oxidation behavior of plasma-sprayed NiCrAlY, the usual bond-coat alloy type used beneath oxide ceramic thermal barrier coatings for gas turbine engine applications. The laser treatment has the surprising effect of concentrating aluminum at the top surface, thus affecting the formation of a protective layer of alumina during oxidation. This characteristic, together with the sealing of pores, provides effective protection at high temperatures.

Evaluating the quality of thermal-sprayed coatings is a major problem. More particularly, industry is seeking means of nondestructive evaluation (NDE) for thermal-sprayed coatings; the NDE techniques should yield quantities that can be related to spray processing parameters. For example, researchers reported attempts to assess adhesion strength through the use of ultrasonics, acoustic emission, and thermography. While industry has indeed driven such studies, little methodology is available to lead in a straightforward manner to useful shop-located devices. Certainly the thermal scanning NDE approach pioneered by Hanford researchers and the US Navy shows the occurrence of non-bonds under aluminum non-skid coatings. But it may be some time before such a device is useful in the field and affordable.

Further work on infrared thermography was reported by Polish and French workers. They demonstrated the feasi-

bility of using infrared thermography to evaluate the surface temperature of the coating during spraying. Such information is useful for a fundamental understanding of processing and, potentially, for on-line process control. It is interesting that no complexities are encountered during temperature measurement of the surface, because the plasma flame has an infrared spectrum sufficiently removed from that associated with the surface of the coating.

More exotic, but no less significant, is the acoustical-optical holography approach reported by workers from the Univ. of Dortmund. The optical fringe technique is combined with ultrasonics, effectively enabling the imaging of the ultrasonic surface wave. Distortions, arising from poor bonds and related faults, thus can be imaged and characterized.

Passive ultrasonic methods and active acoustic emission approaches have been used by workers at SUNY-Stony Brook to evaluate thermal-sprayed metal and oxide coatings. In one study, time-domain analysis was performed on flame-sprayed coatings to characterize a 1-cm² region of poor bonding (achieved by masking during grit blasting). The ultrasonic pulse-echo method yielded good response from the debond region. The extent to which the method can be used to characterize a small defect has not yet been evaluated. In another study, the structural integrity of thermal barrier coatings was evaluated by acoustic emission (AE) techniques. The AE transducer was attached to a tensile adhesion rig, and noise was monitored while the coating was pulled off. Not surprisingly, a relation was noted between the tensile adhesion strength and the cumulative AE counts.

Workers from the Univ. of Aston (Birmingham, UK) studied how process parameters can influence the shear adhesion strength of a range of arc-sprayed coatings. The results indicated that it was not feasible to make realistic, specific recommendations. However, the researchers were able to generalize about how bond coating leads to improved

mechanical properties through a reduction in "the adverse effect of coatings stresses and defects...."

Several papers on quality and its control discussed how processing affects coating properties. H. Drzeniek et al. (Technical Univ. of Wroclaw, Poland) elegantly told the attendees what they already knew: the spray parameters, which are interrelated in complex ways, control the coating properties. A factorial analysis approach was developed to evaluate the complex mathematical concepts connecting the process parameters. The goal, of course, is to establish a practical number of tests to determine the connections. The results appear to open the way to relatively simple relations, which the workers would like to see applied industrially.

A paper from the Centre d'Études Nucléaires de Grenoble reported on the use of factorial two-level experiments to assess the influence of spray parameters on the properties of low-pressure plasma-sprayed MCrAlY coatings. Dekumbis et al. used a statistically optimized approach to take into consideration interactions among the numerous controllable parameters, and at the same time to keep experimentation to a minimum. The researchers considered the following spray process independent variables: spray distance, chamber pressure, current, gas flow, powder feed rate, and substrate preheat temperature. The target-related, generally dependent variables considered were: target weight increase during spraying, coating thickness, deposition efficiency, maximum sample temperature, powder chemistry, coating Vicker's hardness, coating roughness. The report was comprehensive and should be examined by serious sprayers. Target variables were predictable, in general, from the independent spray parameters. One can see this aspect of spray analysis contributing to the rapidly evolving field of automated spraying.

The above papers pointed out one thing clearly: more process research is needed. M. Vardelle et al. (Université de Limoges, France) have done such work.

As part of a long-term and well-supported effort, P. Fauchais and co-workers at Limoges have been studying the velocity and temperatures associated with the direct current (DC) arc plasma jet. It took \$1.5 million, and good science, to achieve the measurements. As pointed out in the conference paper, measurements of particle velocities and temperatures (and their distributions) within the plasma are very useful to an understanding of the process. (I would go a step beyond and say the measurements are essential.) The French have used such numbers, together with computer simulation of plasma-particle momentum and heat transfer considerations, to come up with rather realistic models. Obviously, their contentions must be tempered with the usual realities, such as vaporization and turbulence, but the Limoges experiments and their analyses are thought-provoking and may lead to new ideas, equipment, and processes.

Of the 80 papers presented, less than 10% involved sprayed oxides, and only five of these addressed the question of the usefulness of thermal spraying for producing thermal barrier coatings (TBC). This apparent lack of interest in thermal barrier coatings is rather surprising. Certainly TBCs are not ignored at thermal spraying and ceramics conferences in the United States, where NASA-Lewis has pioneered and encouraged studies of yttria partially stabilized zirconia coatings.

TBCs are receiving well-deserved attention because they can act as thermal insulators for superalloy turbine blades. Increases in operating temperatures can yield improved fuel efficiency; thus, there is great incentive to develop TBCs that can withstand the high temperatures and thermal cycling experienced by such mechanical systems. Zirconia, having low thermal conductivity, is an ideal choice for the TBC, but unfortunately it undergoes allotropic phase transformations during thermal cycling. But yttria, as well as other rare earth oxides, can be used to stabilize the high temperature cubic phase so that the crack-inducing trans-

formations are limited. In fact, NASA-Lewis has demonstrated that partial stabilization (versus complete stabilization of the high temperature cubic phase) of ZrO_2 with 7 to 9 weight percent Y_2O_3 yields a superior TBC, which can withstand considerable thermal cycling. It has been suggested that the effectiveness of the partially stabilized system originates from partial transformation, limiting crack propagation and thus leading to toughening.

TBC systems need to be studied from the point of view of their thermal and transformation properties as related to mechanical behavior. C. Berndt and H. Herman (SUNY-Stony Brook) presented a paper on thermal expansion anisotropy (i.e., parallel versus normal to the surface) of Y-stabilized zirconia and the relationship with stress-induced coating failure on thermal cycling. Like Berndt and Herman, N. Iwamoto et al. (Welding Research Institute, Osaka Univ., Japan) used diffraction methods to do phase studies of zirconia TBCs. The Japanese group also reported on x-ray photoemission spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) studies of zirconia TBCs and developed support for using yttria as the stabilizing agent (versus CaO).

Another aspect of TBCs is their potential as a fire barrier, an application useful on US Navy ships. SUNY-Stony Brook workers reported on the effectiveness of thermal-sprayed oxide coatings to limit (that is, slow down) the melting of aluminum ship plate during a fire. Actually, a flame-sprayed cermet TBC (zirconia or alumina, combined with NiAl) was used and, in fire tests, significantly slowed substrate melting.

The properties of thermal-sprayed coatings were addressed in a number of papers. Workers from the Univ. of Nottingham and industrial colleagues studied the internal stresses associated with electric-arc sprayed steel coatings. Interesting effects of voltages and air pressures on the measured stresses were noted, with higher volt-

ages and decreased air pressures causing increased stresses. A related paper by J. Wagner and Z. Kminek (Prague, Czechoslovakia), concerned the stability of the arc spray process. They related electrical control to coating properties. German workers from the Univ. of Dortmund carried out high speed photography of the electric arc and flame spray processes, seeking to optimize the spray parameters. Such tedious but exciting work, in this writer's opinion, can ultimately lead to major improvements in spray processes. After one has seen the films, it is obvious that new guns can be developed, and established systems can be much improved with high speed photography. (Researchers at SUNY-Stony Brook have taken high speed films of the plasma spraying process. The results are very dramatic, and even at worst convey a better understanding of the spray process. At best, such approaches may be used to improve nozzle design or to understand and modify power supply characteristics.)

Residual stresses of sprayed coatings were the subject of a study by U. Szieslo (Waldems, West Germany), who examined arc- and flame-sprayed hollow cylinders of various ferrous alloys. Both tensile and compressive stresses obtain and, not surprisingly, transformation stresses play a significant role in stress values.

When there are residual stresses, fatigue must be considered. Fatigue properties of a work piece have traditionally been thought to have been degraded following thermal spraying. Thus, workers from Bath Univ. (UK) studied the effect of flame sprayed coatings on the fatigue behavior of high strength steels. The key considerations are heat input and residual stress pattern (tension versus compression). Weakening of the substrate steel through annealing is obviously not beneficial. Again, process variables are the key to how the coating system will be influenced by the sprayed coating.

In another fatigue study, W. Bertram and M. Schemmer (AEG-Telefunken, West Germany) examined flame, plasma,

and D-gun spraying of a range of materials and related residual stresses to the affected fatigue behavior. Again, generalizing is not easy, though it appears, at least for the cases studied by Bertram and Schemmer, that thermal spraying itself (e.g., heating) does not contribute to a degradation of fatigue life. On the other hand, pores, residual stresses, and cracks within the coating will decrease fatigue life. This area of research needs considerable attention.

The US Navy began to flame and arc spray aluminum several years ago for corrosion protection aboard ship. Due to strong incentives and considerable faith in the process, Navy workers have had considerable success in using thermal-sprayed active metal coatings for corrosion protection. (In fact, the Navy's experience has been evaluated by a committee of the National Materials Advisory Board in a recent publication entitled *Metallized Coatings for Corrosion Control of Naval Ship Structures and Components*, Report Number NMAB-409 [1983]. The report is available from DTIC, Alexandria, VA 22314.) It was thus with considerable interest that the conference received a 1983 update from the Naval Sea Systems Command and the David Taylor Naval Ship R&D Center, Annapolis, MD, on the US Navy's recent activities in corrosion control and machine element repair. Examples of

major and minor successes were reviewed, from valve housings to non-skid decks, and work on quality control (NDE), training, and certification was described.

Taking the systems approach to corrosion control and bringing to the problem the entire arsenal of the corrosion engineer, with no prejudice or preconceptions, the US Navy has shown that the syndrome of rusting steel and failing parts does not have to be a way of life, and that sailors on long voyages do not have to be locked in the classic, inefficient, chip-and-paint cycle. Thus the Navy has led the way for American industry; Europeans know the game and use thermal spray readily for marine, transportation, and industrial corrosion control (see ONR London Conference Report C-4-80).

ITSC-83 was a dynamic and interesting conference. One was left with the impression that the technology of thermal spraying is attempting to move from trial and error to a true engineering activity. The practitioners are more sophisticated, are tackling tougher problems, and, most importantly, are achieving increased acceptability in industry. For readers who want a closer look at thermal spraying, a version of ITSC-83 will be held in San Diego in April 1984, as part of the 11th International Conference on Metallurgical Coatings.

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APPENDIX:
SPEAKERS AND PAPERS

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Future Aspects of Thermal Spraying.

H.H. Vanderveldt, R.A. Sulit
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Industrial Thermal Spray Processes
in the U.S. Navy--1983 Update.

A. Grubowski
David W. Taylor Naval Ship R&D Center
Annapolis, MD

W. Milewski, M. Sartowski
Institute of Precision Mechanics
Warsaw, Poland

Some Properties of Coatings Plasma-
Sprayed from NiCrBSi Materials.

Y. Inui, T. Ikuta, R. McDonald,
T. Hayami, M. Nakazaki
Department of Mechanical Engineering
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Osaka, Japan

Study on Grinding of Self-Fluxing
Alloys of Ni and Cr System.

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Aachen

On NiCrBSi Matrix-Carbide Reactions
in Furnace Densified Wear Resistant
Overlays.

N. Iwamoto, Y. Makino, N. Umesaki,
S. Endo
Welding Research Institute of Osaka
Univ.
Osaka, Japan

The Effect of Pretreatments of
Metals on Bond Adhesion.

H. Herman, H. Bhat, R.A. Zatorski
Materials Science Department
State Univ. of New York
Stony Brook, NY

Laser Treatment of Plasma-Sprayed
Coatings.

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Hanford Engineering Development
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Thermal NDE Method for Thermal
Spray Coatings.

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Puget Sound Naval Shipyard
Bremerton, WA

R.A. Sulit
Naval Sea Systems Command
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H.A. Crostack, A. Kruger, W. Fischer
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Nondestructive Testing of Thermal
Sprayed Coatings Using Optical
Holography to Receive Ultrasonic
Waves.

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L. Pawlowski
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Metallurgy of Rare Elements
Technical Univ. Wrocław
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The Application of Infrared Thermo-
graphy in Testing the Coatings and
Optimizing the Plasma Spraying
Process.

Ch. Martin, P. Fauchais
Laboratoire de Thermodynamique
U.E.R. Sciences
Université de Limoges
Limoges, France

H. Bhat, R.A. Zatorski, H. Herman
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Ultrasonic Analysis of Flame-
Sprayed Coatings--Time Domain
Frequency Analysis.

N.R. Shankar, C.C. Berndt, H. Herman
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Engineering
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Stony Brook, NY

Structural Integrity of Thermal
Barrier Coatings by Acoustic
Emission Studies.

L.W. Crane, C.L. Johnston, D.H. James
Department of Metallurgy and
Materials Engineering
Univ. of Aston in Birmingham
Birmingham, Great Britain

Effect of Processing Parameters on
the Shear Adhesion Strength of
Arc Sprayed Deposits.

H.E. Drzenick, A.K. Sikorski,
R. Kaczmarek
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Technical Univ. of Wroclaw
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Optimization of Plasma Spraying
Parameters.

P. Nolle
Schweißtechnische Lehr--und
Versuchsanstalt des DVS
Fellbach

Instruction of Personnel for
Thermal Spraying According to the
Guidelines of the German Welding
Society (DVS).

J. Tragnan
Societe Nouvelle de Metallisation
Industries
Paris, France

Training of Personnel for Thermal
Spraying.

H. Roos
BASF Aktiengesellschaft
Ludwigshafen/Rhein

Production of Air-Polluting Substances
During Plasma Spraying--Measurements
in the Shop by Local and Personal
Air Sampling.

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Factors Influencing the Properties
of Plasma-Sprayed Layers.

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Metallurgical Interaction of Mo and
Steel During Plasma Spraying.

Guo-Chang Jiang, Nan-Gue Liu,
Zhu-Ming Fei
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and Engineering
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A Theoretical Analysis About
Thermal Spraying of Mixed Powders.

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Institute for Problems of Materials
Science
Academy of Sciences of the Ukrainian SSR
Kiev, USSR

Interaction Kinetics in Particles
of Composite Powders During Plasma
Spraying.

F. Kassabji, F. Tourenne, A. Derradji,
P. Fauchais
Laboratoire de Thermodynamique
U.E.R. Sciences
Universite de Limoges
Limoges, France

Aluminium and Aluminium Nitride
Deposition by Low Pressure Nitrogen
Arc Plasma Spraying.

O.V. Roman, P.A. Vityaz, A.N. Babaevsky
Byelorussian Powder Metallurgy Association
Minsk, USSR

Peculiarities of Spraying Coatings
With a Radio-Frequency Induction
Plasmatron.

M. Vardelle, A. Vardelle, P. Fauchais
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U.E.R. Sciences
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Study of the Trajectories and
Temperature of Powders in a D.C.
Plasma Jet--Correlation With
Alumina Sprayed Coatings.

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Fordertechnik, Hochschule der
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Hamburg

Advanced High Velocity Thermal
Spraying of Metallic and Ceramic
Powders.

W. Jurgens
Lufthansa AG, Hamburg

New Trends in the Automation of
Thermal Spray Systems.

P.C. Wolf
Metco Inc.
Westbury, NY

K.D. Borbeck
Plasma-Technik AG
Wohlen, Switzerland

Robotics and Manipulators for
Automated Plasma Spraying and
Vacuum Plasma Spraying.

D. Marantz
Flame-Spray Industries, Inc.
Port Washington, NY

Thermal Spray Powders Produced by
Molten Metal Arc Spray.

Ke Song Zhou, H. Herman
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Sh. Kitahara, I. Okane
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Saarbrücken

Ceramic Based Composite Material
for Flame Spraying.

Influence of Phosphorus on Properties
of Plasma-Sprayed Ni-Al Layers.

Problems of Maintaining the Quality
of Thermal Spray Powders.

Application of Thermal Spraying
in the Nuclear Field.

Economical Hard Surfacing by Flame
Spraying and Flame Fusing of Metal
Powders.

S. Akira
Komatsu Ltd.
Manufacturing Engineering Research Center
Osaka, Japan

Plasma Spraying Anti-Abrasion Parts.

C. Roy
Centre de Recherches de Royallieu
Compiègne, France

An Improved Protective Coating for
Blast Furnace Tuyers and Bush Plates.

S. Dallaire
National Research Council
Industrial Materials Research Institute
Montreal, Canada

H. Drzeniek
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Technical Univ. of Wrocław
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Introduction of Cord Wires to
Arc Spraying.

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Pre-Placement of Braze Filler
Materials by Plasma Arc Spraying.

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Device for Automated Arc Spraying
of Internal Surfaces of Glass Pipes.

A. Sickinger
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Development of Thermal Spray Layers
as Gas Path Seals for Aircraft
Turbine Engines.

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The Stability of the Arc Spray
Process.

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Optimization of Electric Arc and
Flame Spraying Conditions by
Application of High-Speed
Cinematography.

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M. Villat, R. Dekumbis, P. Huber
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MCrAlY Plasma Sprayed Coatings:
Factorial Two-Level Experiments as
an Aid to Determine the Influence
of Spraying Parameters on Coating
Properties.

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Versuchsanstalt für Luft- und
Raumfahrt e.V. (DFVLR)
Institut für Technische Physik
Stuttgart

Low Pressure Plasma Spraying--An
Interesting Method to Produce
Electrodes for Water Electrolysis.

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Coatings Service Division
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